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Multi-scale modelling of membrane distillation: some theoretical considerations

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Abstract

Firstly it is shown that the effective thickness of the membrane is the sum of the actual thickness, k_0/U_L and $\lambda C/U_L$ where k_0 is the thermal conductivity of the membrane matrix, λ is the latent of vaporization of water, C is a parameter (defined as flux per unit thickness of membrane per unit of temperature driving force) and U_L is a coefficient combining the feed side and permeate side film heat transfer coefficients. For typical conditions the sum of the additional terms exceeds 100 μ m which clearly shows that the flux is not inversely proportional to membrane thickness. Also to a first approximation the thermal efficiency is independent of membrane thickness. This work and the development of an overall mass transfer coefficient for direct contact membrane distillation build upon the pioneering work of Giulio Sarti. Secondly a re-assessment of the traditional method for combining the Knudsen diffusion coefficient and the molecular diffusion coefficient suggests that the traditional sum of resistances approach engages in some double counting and thereby overestimates the resistance and consequently underestimates the flux.

Introduction

Writing in the mid 1990's, Lawson and Lloyd¹ noted that many researchers were devoting their efforts towards determining new applications for membrane distillation (MD) in areas where the benefits of MD, especially the high rejection and low operating temperatures, made the process attractive. They drew a contrast with desalination applications. Now whilst MD is currently not a viable alternative to RO it is certainly viewed as a potential alternative especially in conjunction with solar energy and/or for decentralized treatment of brackish waters. This renewed interest is reflected in the developing literature including two recent reviews^{2,3}.

With this renewal of interest, it is timely to address the following questions:

- (i) What is the appropriate expression for the overall mass transfer coefficient, K_{eff} from bulk feed to bulk permeate?
- (ii) Is the value of K_{eff} useful for module design?
- (iii) At the pore scale, what is the correct expression for diffusion in the transition regime where both Knudsen diffusion and molecular diffusion are important?

So firstly there will be a re-examination of the linear model for MD of Gostoli, Sarti & Matulli⁴ and consideration given to thermal efficiency, i.e. whether a compromise has to be made between a thinner membrane favouring the desired high mass transport of vapour (but also a greater heat flux), and a thicker membrane limiting heat loss (but also reducing mass transport). The interesting question, "What is the limiting flux as the membrane thickness tends to a small value of the order of 10 μ m?" is also addressed towards the end of the paper. Prior to that, the second question is discussed. Thirdly the current method for combining the Knudsen diffusion coefficient and the molecular diffusion coefficient will be re-assessed starting from basic kinetic theory.

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There are four main MD configurations namely, direct contact (DCMD), air gap, vacuum and sweeping gas MD. The first part of this paper is concerned with DCMD because of the desire to link to some of Sarti's work⁴, because DCMD has the simplest design and because the method introduced can be extended. In DCMD, both sides of the membrane are in contact with liquid; the aqueous feed on one side and the liquid permeate on the other. The permeate flux across the membrane in any MD system depends not only on the properties of the membrane (including pore size, pore size distribution, porosity and thickness of the membrane)^{1,3} but also on the heat transfer coefficients and the thermal conductivity of the membrane. In the case of DCMD, the film heat transfer coefficients for both the feed side and the permeate side are important, as illustrated in Figure 1. An interesting question is: "What is the limiting flux as the membrane thickness tends to a value say one order of magnitude larger than the maximum pore diameter?" The answer will be provided later.

Development of an overall MD mass transfer coefficient, K_{eff}

Symbols are similar to those used previously⁴. Consider a small section of a module. There are three expressions for the heat flux. Respectively for DCMD: heat transfer across/through the membrane; to the membrane from the bulk feed; and from the membrane to the bulk permeate. The flux through the membrane is N .

$$Q = Q_c + N\lambda \quad (1)$$

$$Q = h_1(T_f - T_{fm}) \quad (2)$$

$$Q = h_2(T_{pm} - T_p) \quad (3)$$

Symbols have their usual meaning and are listed in the Nomenclature. One can allow for the salinity of the feed in terms of a correction to the temperature driving force and for sufficiently small temperature differences across the membrane, the driving force of the partial pressure difference in water vapour pressure can be linearly related to the difference in temperature, $\Delta T = T_{fm} - T_{pm}$ and ΔT^{BP} . The effective driving force is⁴: $\Delta T - \Delta T^{BP}$, and the flux is given by:

$$N = K(\Delta T - \Delta T^{BP}) \quad (4)$$

where K is the flux of water vapour through the membrane per unit of temperature difference across the membrane.

As it is desirable to relate the flux at a particular point in a module to the local difference in bulk temperatures, an overall MD mass transfer coefficient, K_{eff} is defined.

$$N = K_{eff}(\Delta T_b - \Delta T_b^{BP}) \quad (5)$$

where K_{eff} is the flux of water vapour through the membrane per unit of temperature difference between the bulk liquids and ΔT_b is the corresponding local bulk temperature difference.

For ease of exposition, salinity will be ignored (i.e. $\Delta T_b^{BP} \approx 0$) and two heat transfer coefficients will be defined:

$$U_L = (1/h_1 + 1/h_2)^{-1} \quad (6)$$

$$U = \left(\frac{1}{h_1} + \frac{\delta}{k_o} + \frac{1}{h_2} \right)^{-1} \quad (7)$$

The overall thermal conductivity k_o depends upon the thermal conductivity of the polymer, the thermal conductivity of the vapour/gases in the pores of the membrane and the porosity of the membrane. Khayet³ mentions alternative expressions for calculating k_o .

Now from (2) and (3): $Q(1/h_1 + 1/h_2) = (T_f - T_p) - (T_{fm} - T_{pm}) = \Delta T_b - \Delta T$
i.e. $Q = U_L(\Delta T_b - \Delta T)$ (8)

In other works one might find $(T_f - T_p)$ written as $(T_{b1} - T_{b2})$.

Also $Q = \frac{k_o}{\delta} \Delta T + N\lambda$ (9)

Combine (8) and (9) to obtain an equation in ΔT_b and ΔT :

$$\left(\frac{k_o}{\delta} + U_L\right) \Delta T = U_L \Delta T_b - N\lambda \quad (10)$$

From (4) and (5) with $\Delta T_b^{BP} = \Delta T^{BP} = 0$,

$$K\Delta T = K_{eff}\Delta T_b \quad (11)$$

Combining (10) and (11) and eliminating ΔT_b ,

$$K\Delta T = K_{eff} \left[\left(\frac{k_o}{\delta} + U_L\right) \frac{\Delta T}{U_L} + \frac{N\lambda}{U_L} \right] \quad (12)$$

But $N = K\Delta T$ (13)

$$\therefore K = K_{eff} \left[\left(\frac{k_o}{\delta} + U_L\right) \frac{1}{U_L} + \frac{K\lambda}{U_L} \right] \quad (14)$$

Hence $\frac{1}{K_{eff}} = \frac{1}{K} \left[\frac{k_o}{\delta U_L} + 1 \right] + \frac{\lambda}{U_L}$ (15)

By recognising that K is inversely proportional to δ , one can define C (which is the flux per unit thickness of membrane per unit of temperature driving force) and obtain an informative expression for K_{eff} .

$$K = C/\delta \quad (16)$$

$$\therefore \frac{1}{K_{eff}} = \frac{1}{C} \left[\frac{k_o}{U_L} + \delta \right] + \frac{\lambda}{U_L} \quad (17)$$

Equation (17) shows that the overall MD mass transfer coefficient, K_{eff} is dependent upon the latent heat of the water, the film heat transfer coefficients, the membrane thermal conductivity, k_o , and the term C . Now most researchers find the value of C experimentally but equations for its estimation will be considered in the second half of this paper. It is worth mentioning that C is found to be relatively constant with a change in temperature^{5,6} which is not surprising for reasons given later.

Now as a thinner membrane favours the higher mass transport of water vapour but a thicker membrane limits heat loss, it is interesting to enquire whether the amount of water vapour transported per unit of heat transfer (N/Q) varies with membrane thickness. From equations (5), (9), (11) and (16) and with the approximation that $\Delta T_b^{BP} \approx \Delta T^{BP}$:

$$Q = K_{eff}\lambda(\Delta T_b - \Delta T_b^{BP}) + \frac{k_o}{C} K_{eff}\Delta T_b \quad (18)$$

Combining this with equation (5):

$$\frac{N}{Q} = 1 / \left(\lambda + \frac{k_o}{c} \left[\frac{\Delta T_b}{\Delta T_b - \Delta T_b^{BP}} \right] \right) \quad (19)$$

The porosity of the membrane affects the value of the overall thermal conductivity, k_o , but all terms in equation (19) are independent of the membrane thickness. Therefore within the limits of the approximations made in the development of equation (4), and the assumption that $\Delta T_b^{BP} \approx \Delta T^{BP}$, the overall thermal efficiency is independent of membrane thickness.

Implications derived from the expression for the overall MD mass transfer coefficient, K_{eff}

Now one can re-write equation (17) to express K_{eff} in terms of a numerator that is C , and a denominator that is the sum of terms with the dimensions of length.

$$K_{eff} = \frac{C}{\delta + \left(\frac{k_o}{U_L} \right) + \left(\frac{\lambda C}{U_L} \right)} \quad (20)$$

Some typical values for parameters for equation (20) and an illustration of the importance of the terms other than membrane thickness in determining K_{eff} are shown in Table 1 and Figure 2. Gostoli et al⁴ concluded that for very low values of membrane thickness, say $\delta \ll k_o/U_L$, then the overall MD mass transfer coefficient, K_{eff} , becomes independent of delta and so does the flux for the pure water case. This accords with equation (20) but it can be noted that the third term in the denominator, $\lambda C/U_L$, is as important as k_o/U_L . Any estimates of optimum thickness need to be made for a specified salinity and in the absence of feed side salinity the above equation agrees with the observation in a recent review³ that experimental results indicated a reduction of the permeate flux with an increase of membrane thickness.”

The plot in Figure 2 of $\frac{1}{K_{eff}}$ vs δ is based on equation (17). It has a gradient $1/C$ and intercept of

$\left(\frac{k_o}{C} + \lambda \right) / U_L$. The results from full matlab simulations for a counter-current flat sheet module were plotted on this basis for various inlet temperatures. A fixed intercept was not obtained (See Figure 3). This illustrates the limitation of assuming equation (5) to be valid for a range of temperatures when diffusion coefficients are a function of temperature and the vapour pressure of water varies non-linearly and is accurately calculated from:

$$P^0 = \exp \left(23.20 - \frac{3816.44}{T - 46.13} \right) \quad (21)$$

where T is measured in Kelvin and P^0 is in Pa.

Whilst equation (20) has its limitations as a design equation, it does illustrate the relative importance of the membrane thickness and shows that there is no optimum thickness unless salinity effects are taken into account. As K_{eff} uses bulk temperatures it will be useful in combination with heat balances when evaluating the required size of a module. In heat exchanger design, pure co-current and counter-current designs can be sized, when there is no phase change, by use of the classic formula: $Q = UA\Delta T_{lm}$. For DCMD an algebraic approach will not be possible but in combination with heat balances, it is anticipated that K_{eff} will be useful when making initial estimates.

The link between equation (17) and equation (16) in Gostoli et al⁴ is now examined. Gostoli et al wrote that

$$\frac{1}{K_{eff}} = \frac{k_o}{KU\delta} - \frac{\lambda}{U_L} \quad (22)$$

Re-writing their equation as an explicit equation in K_{eff} and signifying that we are referring to their expression by introducing the superscript GSM, one obtains:

$$K_{eff}^{GSM} = \frac{KU\delta U_L}{U_L k_o - \lambda KU\delta} = \frac{K\delta U_L}{\frac{U_L}{U} \cdot k_o - \lambda K\delta} \quad (23)$$

Now from equations (6) and (7) one obtains: $\frac{1}{U} = \frac{1}{U_L} + \frac{\delta}{k_o}$ (24)

Combining equations (23) and (24) one obtains:

$$K_{eff}^{GSM} = \frac{K\delta U_L}{\frac{U_L}{U} \cdot k_o - \lambda K\delta} = \frac{K\delta U_L}{k_o \left(1 + \frac{\delta U_L}{k_o}\right) - \lambda K\delta} = \frac{K\delta U_L}{k_o + \delta U_L - \lambda K\delta} = \frac{K}{\left(\frac{k_o}{\delta U_L}\right) + 1 - \left(\frac{\lambda K}{U_L}\right)} \quad (25)$$

However returning to our derivation and by eliminating C from (20) by re-introducing K , one can obtain:

$$K_{eff} = \frac{K}{1 + \left(\frac{k_o}{U_L \delta}\right) + \left(\frac{\lambda K}{U_L}\right)} \quad (26)$$

It is seen that equation (25) and (26) differ by the sign in front of the last term in the denominator on the RHS. Tracing back, it is our belief that either a typographical error occurred in the presentation of GSM's equation 16 or there was a slip in their combination of equations equivalent to equations (8) and (9). It is also noted that the final forms presented here do not contain all of U , U_L and k_o in the same equation. This is considered preferable as one can always eliminate one of these in terms of the other two. It is suggested that equation (20) is probably more useful than equation (26) because C is independent of membrane thickness δ .

Combining equations (17) and (6) in order to explicitly introduce h_1 and h_2 would enable one to construct a 'Wilson' plot to investigate the influence of feed flow rate and/or permeate flow rate. Wilson first constructed plots of the reciprocal of the overall heat transfer coefficient vs the reciprocal of the flowrate to the power of 0.8 (assuming turbulent flow) nearly 100 years ago. Fernandez-Seara et al⁷ have provided a general review of the Wilson plot method and its modifications for heat transfer and extensions of these to DCMD should be considered, especially when detailed data is available as in Song *et al*'s⁸ Figure 8.

Expressions for Combined Diffusion: Critique of the literature

Before concentrating upon the appropriate way of combining diffusion coefficients, it is necessary to emphasize that the presence of Knudsen diffusion necessarily excludes the presence of Poiseuille flow. Consider the following equation:

$$N = C^p \Delta P^o \quad (27)$$

The difference in vapour pressure due to the temperature difference across the membrane drives the permeation of water vapour through the pores from the feed side to the permeate side. Various mathematical models for C^p , namely Knudsen diffusion, Poiseuille flow, molecular diffusion and different combinations of these modes have been developed but it is wrong to assume that for a given pore one can have all three. In particular the combination of Knudsen diffusion with viscous flow is a

contradiction in terms and physically invalid. This has not always been appreciated; see for example the 4th entry in Table 4 in Curcio & Drioli², and comments elsewhere^{1,3} on the transition regime. As explained by Tabor⁹ the concept of viscous flow of a gas is only valid if the mean free path of the gas, Λ , is very small compared with the dimensions of the channel, i.e. Knudsen number Λ/d is very small (here d is the characteristic dimension of the channel such as the gap between plates or the pipe diameter). Now when the mean free path of the gas, Λ , is an appreciable fraction of d , there will be a reduction in the apparent viscosity of the gas by a factor f ,

$$f = \frac{d}{d+2\Lambda} \quad (28)$$

If $\Lambda \approx d$ or greater then Tabor⁹ makes it clear that the concept of a viscosity is no longer valid for the nature of the flow; the necessary continuum hypothesis for this concept no longer holds. This point, which is illustrated in Figure 4, has been made firmly because of continuing misunderstanding in the membrane community.

It is also beneficial to examine the derivation of the diffusion coefficient from first principles. Tabor⁹ shows that the coefficient of self-diffusion is given by:

$$D = \frac{\bar{c}}{3\pi n\sigma^2} \quad (29)$$

where \bar{c} is the mean speed of a gas molecule, n is the number of molecules per m³, and σ^2 is the molecular cross-section.

As n is proportional to pressure P (and inversely proportional to T) equation (29) indicates why $D.P$ is taken to be a constant. This result is also obtained from the more accurate Chapman-Enskog kinetic theory¹⁰. Incidentally one needs to start with the latter to explain clearly why the diffusion coefficient increases roughly as the 2.0 power of temperature, T as equation (29) suggests a 1.5 power if σ^2 , the molecular cross-section, is taken to be constant. Just as a more in depth examination of the effect of temperature suggests a refinement, a more in depth examination of molecule-molecule interactions shows that D is evidently reduced by molecular collisions as determined by n and the molecular cross-section σ^2 . So it is the number of molecular collisions and not the pressure per se that determines the value of the diffusion coefficient.

The traditional approach assumes that the resistances of the molecule-molecule interactions and the molecule-wall act in series with each other but it is contended here that the influence of the former must be reduced as the influence of the latter increases. So if at any instance a fraction of molecules (θ) is moving through a pore by Knudsen diffusion, then only that fraction $1 - \theta$ is experiencing molecule-molecule interactions. Thus the effective value of n in equation (29) is reduced by the factor $1 - \theta$. It follows that for a pair of gases, the effective molecular diffusion coefficient D_{ij} is:

$$D_{i,j} = \frac{D_{ije}^0}{P(1-\theta)} \quad (30)$$

It now remains necessary to determine an expression for θ as a function of the Knudsen number, Λ/d . Details are not included here but geometrically arguments suggested that $\theta=1/3$ when $d = 2\Lambda$. The expression given by equation (28) does not satisfy this condition and for diffusion it is suggested that the following approximation is used:

$$\theta = \frac{\Lambda}{d+\Lambda} \quad (31)$$

Expression for Combined Diffusion with weighting to reflect degree of Knudsen transport:

From the above considerations and especially for $Kn > 0.05$, the actual molecular diffusion coefficient should be calculated from:

$$D_{i,j}^{act} = \frac{D_{ij}}{(1-\theta)} = \frac{d+\Lambda}{d} D_{i,j}^{P_T} \quad (32)$$

where $D_{i,j}^{P_T}$ is the molecular diffusion coefficient evaluated at the total pressure P^T .

Whilst one of us might also challenge the linear combination of resistances, the framework of the dusty gas model (DGM) and the combination of resistances shown in Figure 5(b) will be the basis for combining resistances. Surface diffusion can be ignored due to low molecule–membrane interaction¹².

For stagnant air, DGM reduces to¹ :

$$\frac{J_w^D}{D_{Kw}} + \frac{y_a J_w^D}{D_{w,a}^{act}} = -\frac{1}{RT} \nabla p_w \quad (33)$$

The term J_w^D in equation (33) is the mass flux in the pore and y_a is the local mole fraction of air. Allowing for membrane porosity and tortuosity and integrating this equation, one obtains for the mass flux across the membrane:

$$N = \frac{(\varepsilon/\tau)P_T D_{w,a}^{act}}{\delta RT_m} \cdot \ln \left[\frac{D_{Kw}(1-y_{wpm}) + D_{w,a}^{act}}{D_{Kw}(1-y_{wfm}) + D_{w,a}^{act}} \right] \quad (34)$$

where subscripts *fm* and *pm* refer to pore inlet (feed side) and pore exit (permeate side) respectively, as indicated in Figure 1.

Incorporating equation (32), writing $(1 - y_{wpm})$ as y_{apm} and recalling the definition of Knudsen number, equation (34) becomes:

$$N = \frac{(\varepsilon/\tau)P_T(1+Kn)D_{w,a}^{P_T}}{\delta RT_m} \cdot \ln \left[\frac{D_{Kw} \cdot y_{apm} + (1+Kn)D_{w,a}^{P_T}}{D_{Kw} \cdot y_{afm} + (1+Kn)D_{w,a}^{P_T}} \right] \quad (35)$$

Both D_{Kw} and $D_{w,a}^{P_T}$ have units of $m^2 s^{-1}$ and y_a is calculated from knowing the partial pressure of water vapour and the total pressure P_T . This equation can be compared with equation (31) of Khayet³ and with equation (15) of Phattaranawik *et al*¹¹ to ascertain the validity of its form, remembering that herein the expression for D_{Kw} is:

$$D_{Kw} = \frac{4d}{3} \sqrt{\frac{RT_m}{2\pi m_w}} \quad (36)$$

Figure 6 compares some calculated fluxes for given feed inlet temperatures with predictions made assuming (i) only Knudsen diffusion, (ii) only molecular diffusion, (iii) traditional combination of Knudsen diffusion and molecular diffusion, and (iv) equation (35). Whilst equation (35) makes for an improvement, it still gives an underestimate. As discussed by Phattaranawik¹¹, pore size distribution is important and that has yet to be included in our analysis and this might account for part of the discrepancy. Also the tortuosity of the pores is another important factor.

At the pore scale, it is accepted that the water vapour diffusion is in the transition regime where both Knudsen and molecular diffusion are important. Therefore the fact that the results in Figure 6 indicate that the best fit is for the assumption of pure molecular diffusion is taken mainly to be a coincidence. Also it is taken as confirming that the traditional sum of resistances approach engages in some double counting. Now whilst the new approach is theoretically superior, the expression for θ probably needs further refinement.

The main point of the second part of the paper has been to introduce the notion that allowance has to be given to the instantaneous fraction of molecules (θ) that are moving through a pore by Knudsen diffusion and hence are not involved in molecule-molecule interactions. So in concluding this section a comparison between the traditional expression for combined diffusion and the one arising from the above analysis will be made.

The expression arising from DGM¹ can be written as:

$$\left[\frac{1}{D_{Kw}} + \frac{y_a}{D_{w,a}^{PT}} \right]^{-1} = D_{com} \quad (37)$$

A modified version of this can be found in the early part of Khayet's review³ and in the so-called Fickian section of Suwanwarangkul et al's¹² review. The modification, equation (38) is exact for countercurrent equimolar diffusion and is otherwise only an appropriate approximation when y_a tends to unity.

$$\left[\frac{1}{D_{Kw}} + \frac{1}{D_{w,a}^{PT}} \right]^{-1} = D_{com} \quad (38)$$

For simplicity the expression developed herein will be compared to equation (38) and is accordingly written as:

$$\left[\frac{1}{D_{Kw}} + \frac{1}{(1+Kn)D_{w,a}^{PT}} \right]^{-1} = D_{com}^{new} \quad (39)$$

The new expression has been evaluated in two ways. Firstly a comparison is given in Figure 6, using data taken from Cath et al¹⁴ who used well defined channels enabling one to make good estimates of the film heat transfer coefficients. The predictions were made using our standard matlab model with

the effective diffusivities being based on Knudsen alone, molecular diffusion alone, the traditional expression for combined diffusion and equation (35).

Secondly there is a direct comparison of equations (38) and (39). It has been reported that the mean free path of water in air, at the typical membrane temperature of 60 °C, is 0.11 μm ¹⁰. As a temperature of 320K has been used to calculate the data for Table 2, a value of 0.105 μm was used. The molecular diffusion coefficient $D_{w,a}^{P_T}$ was calculated using the empirical formula^{11,14}:

$$D_{w,a}^{P_T} = (1.895 \times 10^{-5}) T^{2.072} / P_T \quad (40)$$

where all units are standard SI units.

Table 2 compares equations (38) and (39) and shows that in the size range of interest the suggested approach predicts a larger value for the combined diffusion coefficient especially in the range 0.05 to 0.3 μm where it is 21% or greater. Both expressions tend to the limits expected, namely D_{Kw} for very small pores and $D_{w,a}^{P_T}$ for very large pores.

At the beginning the question, “What is the limiting flux as the membrane thickness tends to a small value of the order of 10 μm ?” was raised. Recently¹⁵ the mechanisms of gas permeation through single layer graphene have been considered and as they noted Knudsen¹⁶ gave the solution for gas transport through an infinitesimally thin orifice. Comparison these equations with the above equations used herein shows that the flux through a pore, compared with the flux through a 2D atomically thin membrane, will be reduced by a factor of about $4d/3\delta$. Recalling that the pore diameters and the mean free paths in DCMD are a fraction of a micron, it is clear that the pores should still be modeled as 3D even for membranes as thin as 10 μm . The factor $4d/3\delta$ indicates that more advanced modeling is required for pores whose lengths are a few pore diameters or less.

Concluding remarks

The following expression was developed for the overall mass transfer coefficient for direct contact membrane distillation:

$$K_{eff} = \frac{C}{\delta + \left(\frac{k_o}{U_L}\right) + \left(\frac{\lambda C}{U_L}\right)} \quad (20)$$

It shows that the effective thickness of the membrane is the sum of the actual thickness, k_o/U_L and $\lambda C/U_L$. The sum of the additional terms depends crucially upon the film heat transfer coefficients but typically exceeds 100 μm . The analysis, which ignored salinity effects, did not suggest an optimum thickness for flux. However it is known that salinity can, for the combination of a low temperature difference and a thin membrane, lead to a negative flux⁴. So an optimum thickness would exist if salinity were to be taken into account. This would arise because flux across the membrane itself is determined by $\Delta T - \Delta T^{BP}$ whilst heat loss is determined by ΔT . As the membrane becomes thinner ΔT is reduced and becomes comparable with ΔT^{BP} so the flux and the energy efficiency are both adversely affected. Thus for actual DCMD applications, equation (20) should be considered to be an approximation.

With regard to thermal efficiency, it was found that the overall thermal efficiency is, to a first approximation, independent of membrane thickness. If the approximation $\Delta T_b^{BP} \approx \Delta T^{BP}$ were to be replaced by a more accurate expression some weak dependency can be anticipated.

The re-assessment of the traditional method for combining the Knudsen diffusion coefficient and the molecular diffusion coefficient suggested a new expression. This was found to be superior when compared to data but there was still a discrepancy. Now, all comparisons are hampered by uncertainty concerning the tortuosity factor, and unless specific allowance is made for it, by the presence of a pore size distribution. Thus discrimination between two expressions purely on the basis of one comparison with data is not decisive. However it is considered that the traditional sum of resistances approach engages in some double counting and therefore that the new approach is theoretically superior. It indicates that the effective diffusion coefficient in the pore size range of interest for membrane distillation has been underestimated by around 25%. Further theoretical work might indicate that this too, is an underestimate.

Nomenclature		
C	Parameter defined in equation (16)	kg/ m. s K
C^p	Parameter defined in equation (27)	kg/ m ² s Pa
D	Diffusion coefficient	m ² /s
D^0	Pressure independent diffusion coefficient	Pa. m ² /s
d	Diameter of tube or gap between plates	m
h	Heat transfer coefficient	W/m ² K
K	Mass transfer coefficient	kg/ m ² s K
K_{eff}	Overall MD mass transfer coefficient	kg/ m ² s K
k_o	Thermal conductivity of membrane matrix	W/ m K
J^D	Diffusive flux through pore	kg/ m ² s
N	Mass flux across membrane	kg/ m ² s
p^o	Saturated vapour pressure	Pa
Q	Heat flux	J / s
T	Temperature	K
U_L	Heat transfer coefficient defined in equation (6)	W/m ² K
U	Overall heat transfer coefficient	W/m ² K
Λ	Mean free path of gas	m
λ	Latent heat of vaporization	J / kg
δ	Membrane thickness	m
ΔT	Difference in temperature	K
Subscripts		
a	Air	
b	Bulk	
c	Conduction	
f	Feed side (bulk)	
fm	Membrane surface on feed side	
K	Knudsen	
m	Mean	
p	Permeate side (bulk)	
pm	Membrane surface on permeate side	
T	Total	
w	Water	
Superscripts		
BP	Boiling point rise due to salinity	

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Symbol	Dimensions	Illustrative values	Comment
C	$\text{kgm}^{-1}\text{s}^{-1}\text{K}^{-1}$	$30\text{-}170 \times 10^{-9}$	See Figure 2
k_o	$\text{Wm}^{-1}\text{K}^{-1}$	0.1	
U_L	$\text{Wm}^{-2}\text{K}^{-1}$	2000	
δ	μm	100	
λ	kJkg^{-1}	2400	
k_o/U_L	μm	50	
$\lambda C/U_L$	μm	60	Calculate for $C=50 \times 10^{-9}$
$\frac{\delta}{\delta + (k_o/U_L) + (\lambda C/U_L)}$	-	47.6%	Calculate for $C=50 \times 10^{-9}$ and $\delta = 100 \mu\text{m}$
K_{eff}	$\text{kgm}^{-2}\text{s}^{-1}\text{K}^{-1}$	0.000238	ditto
K_{eff} (if $\delta=0$)	$\text{kgm}^{-2}\text{s}^{-1}\text{K}^{-1}$	0.000455	Calculate for $C=50 \times 10^{-9}$

Table 1 Typical values of the parameters for equation (18) and an illustration of the importance of the terms other than membrane thickness in determining K_{eff}

Pore size	Kn	$D_{Kw} * 10^6$	$D_{com} * 10^6$ (Equ 38)	$D_{com}^{new} * 10^6$ (Equ 39)	Ratio D_{com}^{new} to D_{com}
μm		$m^2 s^{-1}$	$m^2 s^{-1}$	$m^2 s^{-1}$	
0.01	10.5	2.0	1.9	2.0	1.06
0.05	2.1	10.2	7.6	9.2	1.21
0.1	1.05	20.4	12.0	15.2	1.27
0.15	0.7	30.7	14.9	18.9	1.27
0.2	0.53	40.9	17.0	21.3	1.25
0.25	0.42	51.1	18.5	22.8	1.23
0.3	0.35	61.3	19.7	23.9	1.21
0.35	0.30	71.6	20.6	24.7	1.20
0.4	0.26	81.8	21.4	25.3	1.18
0.45	0.23	92.0	22.1	25.8	1.17
0.5	0.21	102.2	22.6	26.1	1.16
0.55	0.19	112.5	23.1	26.4	1.15
0.6	0.18	122.7	23.5	26.7	1.14
0.65	0.16	132.9	23.8	26.9	1.13
0.7	0.15	143.1	24.1	27.1	1.12
0.75	0.14	153.4	24.4	27.2	1.12
0.8	0.13	163.6	24.6	27.3	1.11

Table 2 Comparison of the traditional and a new approach for calculating the combined diffusion coefficient. The mean temperature =320K and $D_{w,a}^{PT}=2.90 m^2 s^{-1}$. Mean free path = 0.105 μm

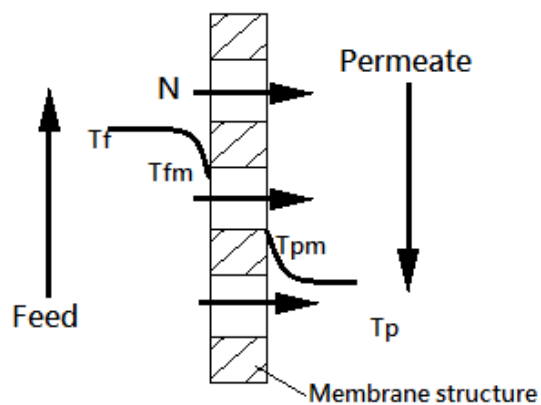


Figure 1 Schematic illustration of the transfer processes across the membrane.

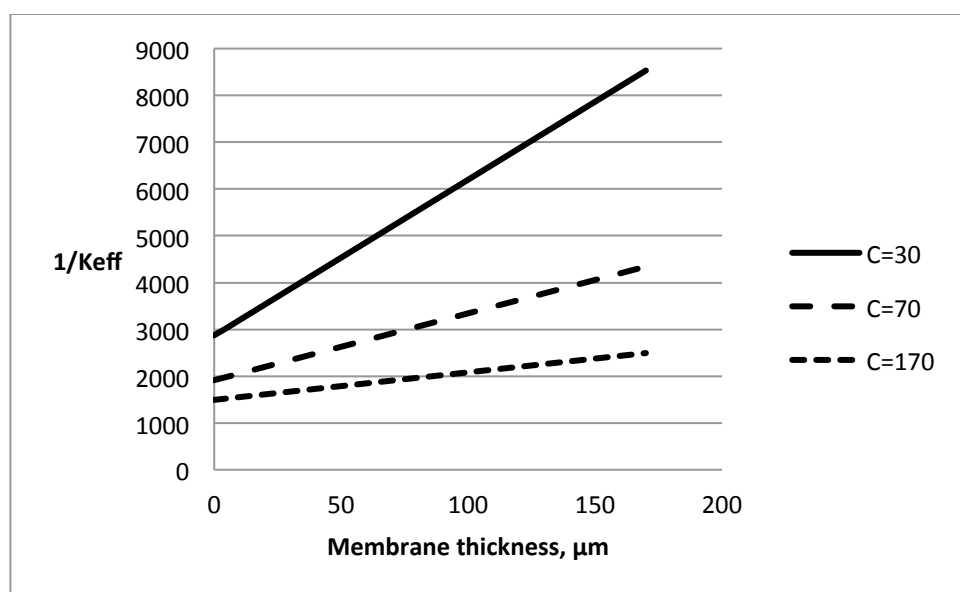


Figure 2 Illustration of the influence of membrane thickness upon the reciprocal of the overall MD mass transfer coefficient for selected values of the parameter C. See Table 1 for units of C.

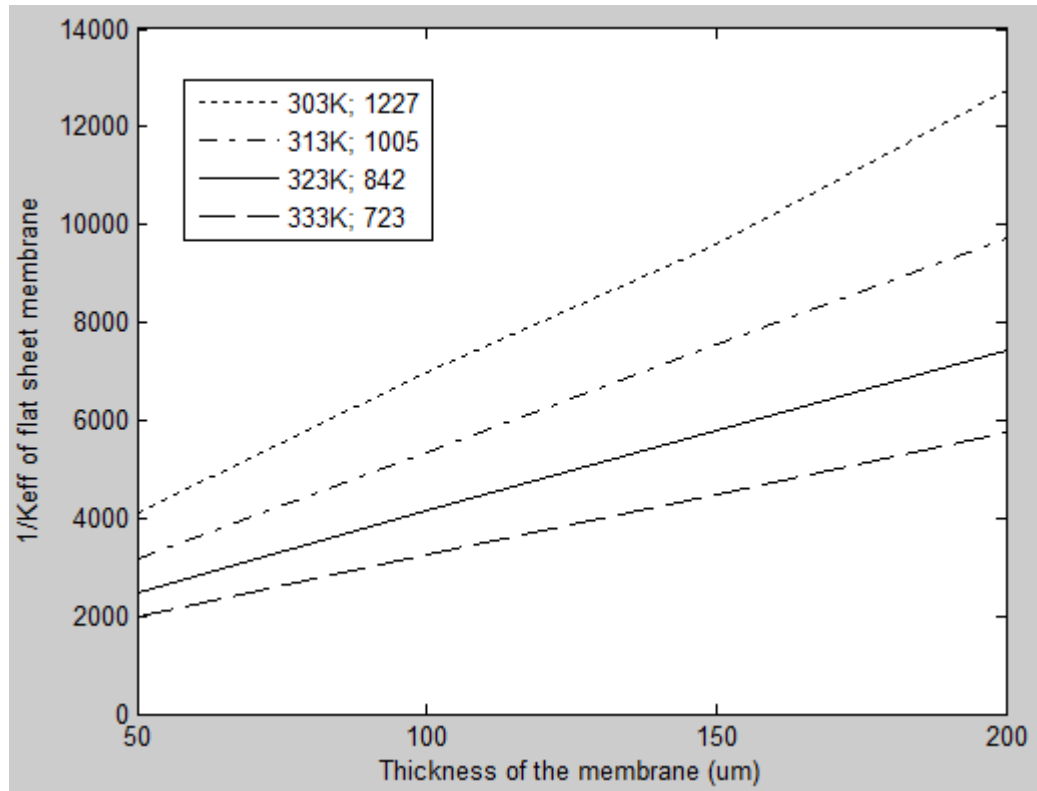


Figure 3 Predicted variation of $1/K_{\text{eff}}$ with membrane thickness for various feed inlet temperatures. The values of the intercept are shown in the legend. The linear approximation of the driving force for vapour transport is seen to have its limitation; the linear theory predicts a common intercept.

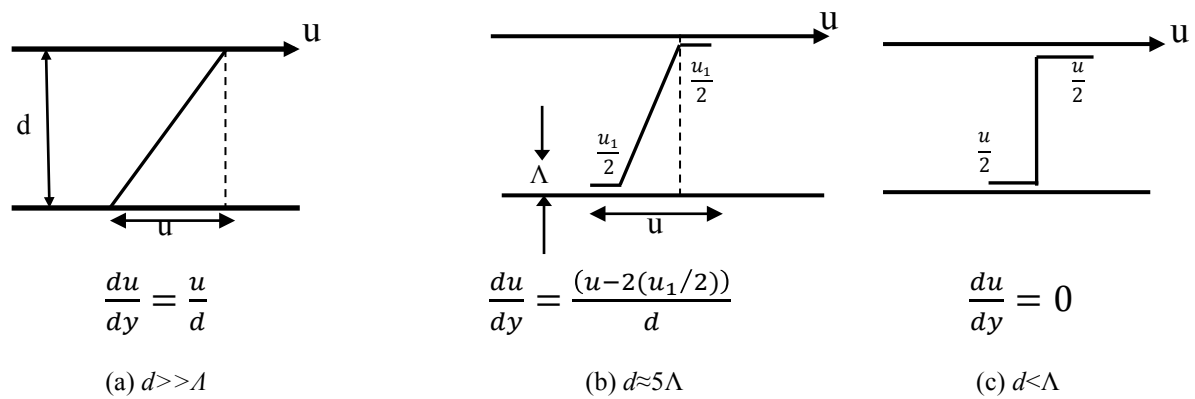


Figure 4 Velocity profiles between two parallel plates, a lower stationary plate and an upper plate moving at velocity u for (a) $d \gg \Lambda$, (b) $d \approx 5\Lambda$, (c) $d < \Lambda$. In (b) there is a reduced gradient due to an effective discontinuity in the mean tangential gas velocity close to the wall. For (c) there is complete slip of $u/2$ at each surface. Adapted from Tabor⁹.

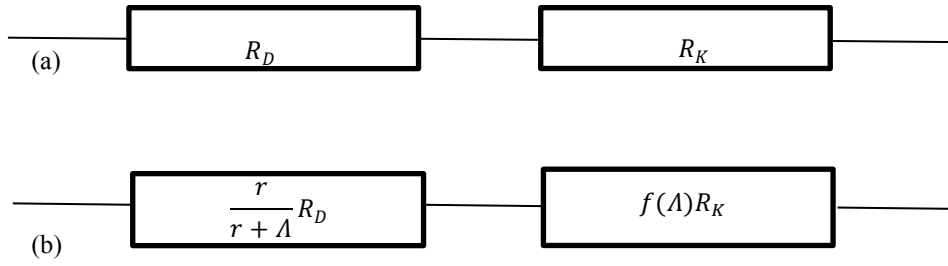


Figure 5 Electrical analogues: (a) traditional presentation; (b) current work. In this paper $f(\Lambda)=1$ and viscous term excluded for reasons given in text.

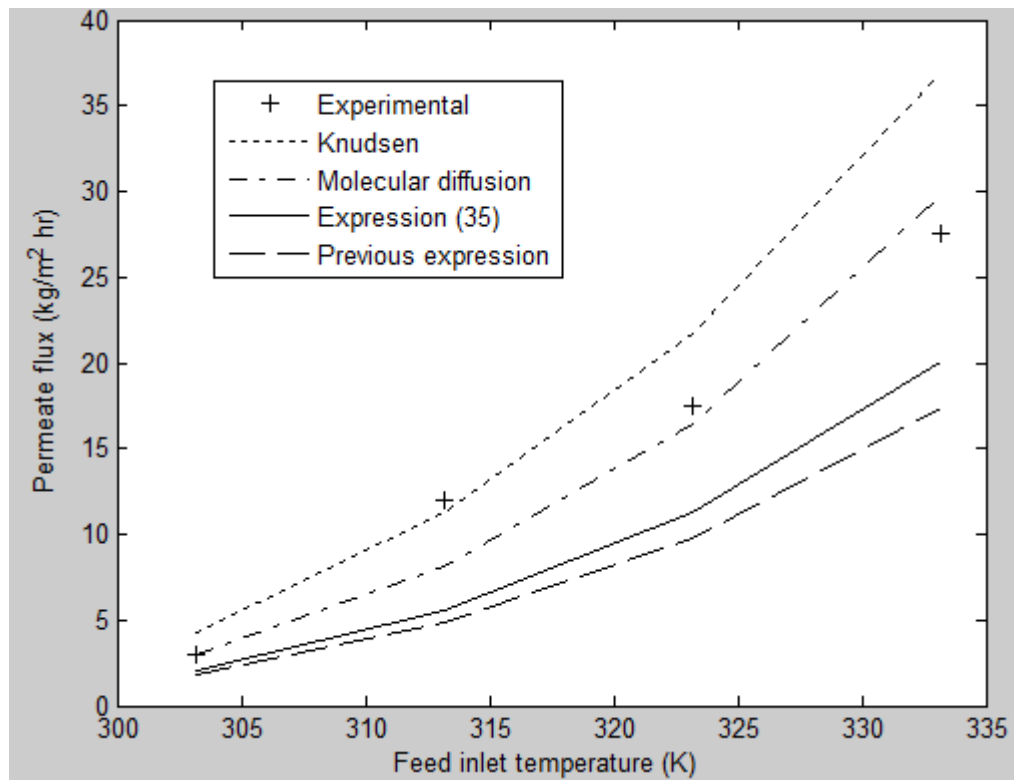


Figure 6 Comparison of data [13] with the assumption of (i) only Knudsen diffusion, (ii) only molecular diffusion, (iii) traditional combination of Knudsen diffusion and molecular diffusion, and (iv) equation (35), which incorporates incorporated the modified θ .